Synthesis and electrochemical properties of fullerene-containing C_{60}—acceptor dyads with fluoronitrobenzene and fluoroquinoxaline moieties as substituents

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Reactions of fullerene C_{60} with 4-azido-3-fluoro-1-nitrobenzene and 7-azido-6-fluoroquinoxaline afforded earlier unknown cycloadducts (C_{60}—acceptor dyads), in which the electron affinities of the fullerene spheres are comparable with the affinity of nonmodified C_{60}.

Key words: [60]fullerene, 4-azido-3-fluoro-1-nitrobenzene, 7-azido-6-fluoroquinoxaline, 1,3-dipolar cycloaddition, electrochemical properties.

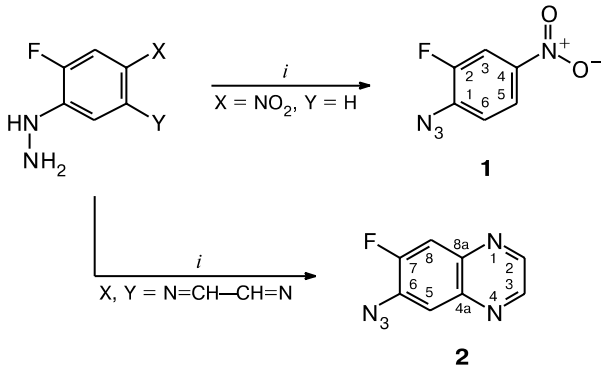
Covalent addition of electron-deficient fragments to the fullerene cage C_{60} is a route to dyads used to create systems essentially operating *via* electron transfer.[1] Among various types of electron-deficient compounds, nitroarenes are believed to be very promising for regulation of the redox properties of the fullerene sphere. It was demonstrated that the presence of nitro- and dinitrophenyl substituents in the exohedral ring of fullerenopyrrolidines makes this molecule closer in electron affinity to nonmodified fullerene.[2,3] In addition, it was found that direct attachment of six nitro groups to the fullerene sphere gives organofullerene $C_{60}(NO_2)_6$, which exhibits stronger electron-withdrawing properties than nonmodified fullerene.[4] An analogous effect of the nitro group on the redox properties of the sphere was revealed in dinitrospirofluorenofullerene.[5] We also showed that the nitropyrimidine fragment in azahomo[60]fullerene[6] and [60]fullereno[1´,2´:4,5]imidazo[1,2-*b*]pyrimidine[7] substantially increases the electron affinity of the fullerene sphere in these compounds.

To fix a nitrophenyl fragment at the surface of the fullerene sphere, we proposed to use well known reactions of fullerenes with organic azides.[8] This method is attractive because of various structures of the fullerene sphere and the exohedral heterocycle in the resulting organofullerenes.

In the present work, we used for the first time fluorinated derivatives of organic azides, namely, 1-azido-2-fluoro-4-nitrobenzene (**1**) and 6-azido-7-fluoroquinoxaline (**2**). Apart from the fluorine atom present in both molecules, azide **1** contains an electron-withdrawing nitro group; in azide **2**, its effect is simulated by the benzoannelated pyrazine ring.

Azides **1** and **2** were prepared by reactions of the corresponding aryl- and hetarylhydrazines with sodium nitrite in an excess of HCl (Scheme 1).

Scheme 1



Reagents and conditions: *i*. H_2O, $NaNO_2$, HCl, 0—3 °C, 0.5—1 h.

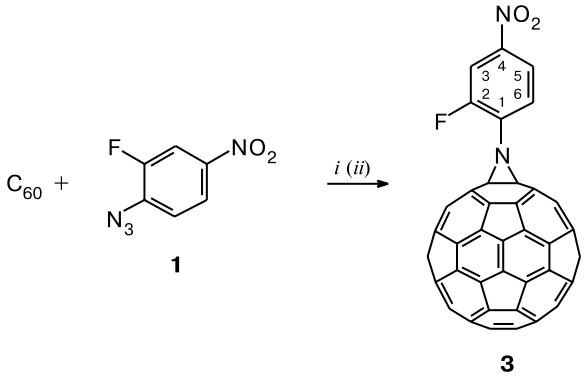
Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 3, pp. 650—655, March, 2005.

1066-5285/05/5403-0660

The structures of azides **1** and **2** were proved by IR, UV, and ^1H and ^{13}C NMR spectroscopy; their compositions were determined by elemental analysis.

The reaction of C_{60} with a double excess of arylazide **1** was carried out in *o*-dichlorobenzene (*o*-DCB) using different temperatures and durations: at 100 °C for 30 h and at 180 °C for 2 h (Scheme 2). The components of the reaction mixtures were separated out by column chromatography with toluene as the initial eluent. According to data from TLC, mass spectrometry, and UV spectroscopy for the separated fractions, the reaction product was compound **3**, regardless of the reaction conditions. An increase in the eluent polarity during chromatography allowed isolation of a mixture of isomeric polyadducts.

Scheme 2



Reagents and conditions: *i*. *o*-DCB, 180 °C, 2 h; *ii*. *o*-DCB, 100 °C, 30 h.

The mass spectrum of cycloadduct **3** (EI) contains the molecular ion peak with *m/z* 874 corresponding to a fullerenoaziridine cycloadduct, in which one molecule of arylazide **1** is attached to the fullerene sphere. The ^1H NMR spectrum of adduct **3** shows signals for the H atoms of the fluoronitrophenyl fragment: a characteristic doublet of doublets at δ 7.81 ($^4J_{H,F} = {}^3J_{H,H} = 8.3$ Hz) for the H(6) atom and a multiplet at δ 8.27—8.23 arising from an overlap of signals for the other H atoms. It should be noted that the signals for the H atoms in cycloadduct **3** are shifted downfield compared to the signals for the analogous H atoms in the starting azide **1** (see Experimental). The largest shift of the signal for the H(6) atom is most likely due to the electron-withdrawing effect of the substituent at the C(1) atom.

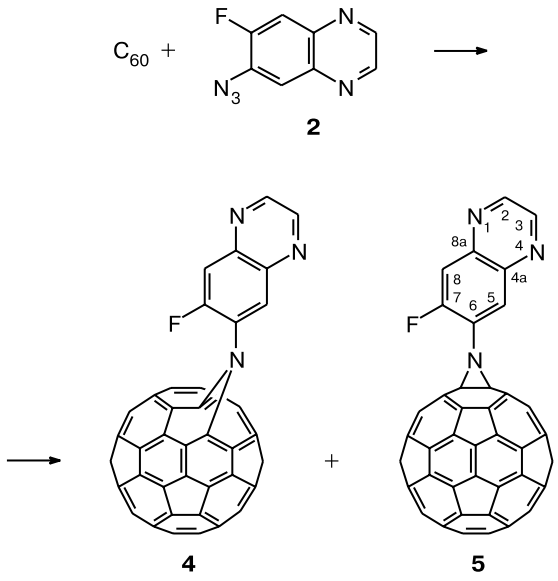
The ^{13}C NMR spectrum of adduct **3** suggests a high symmetry of its molecule. The fullerene sphere of the adduct is manifested by 14 lines (1 — 2 C, 12 — 4 C, and 1 — 8 C) in the δ range from 140 to 145 ppm. Their number and relative intensities indicates symmetry C_{2v}. Theoretically, the spectrum of the sphere should contain three signals with an intensity of 2 C and 13 signals with an intensity of 4 C. Two signals with 2 C and 4 C overlap, probably, because of their close chemical shifts. A singlet for the sp^3-hybridized C atoms of the fullerene sphere appears at δ 84.13, which is characteristic of these C atoms.[8] In the proton-decoupled ^{13}C NMR spectrum of adduct **3**, two broadened singlets for the C(4) and C(6) atoms and four doublets for the C(2), C(3), C(4), and C(6) atoms with the $^{13}C—^{19}F$ spin-spin coupling constant were assigned to the fluoronitrophenyl fragment.

The fullerenoaziridine structure of adduct **3** was also confirmed by UV data. For instance, the spectrum contains broad intense bands with $\lambda_{max} = 255$ and 324 nm, a narrow low-intensity band at 421 nm, and broad low-intensity bands at 457 and 675 nm. These low-intensity bands are characteristic of 6,6-closed adducts.[9]

Thus, the totality of our spectroscopic data suggests that the reaction of C_{60} with 4-azido-3-fluoro-1-nitrobenzene (**1**) yields 1-(2-fluoro-4-nitrophenyl){[60]fullereno[1,2-*b*]}aziridine (**3**) as the monoadduct.

The reaction of C_{60} with azide **2** was carried out in *o*-DCB at 180 °C. Column chromatography of the reaction mixture gave individual products **4** and **5** (Scheme 3). The mass spectra of both products contain the molecular ion peak corresponding to fullerenoaziridine monocycloadducts. However, the UV spectra of adducts **4** and **5** are different. For instance, the spectrum of adduct **5** shows a narrow low-intensity band with $\lambda_{max} = 425$ nm, which is absent from the spectrum of adduct **4**. This suggests that adducts **4** and **5** are 5,6-open and 6,6-closed derivatives of fullerene C_{60}, respectively. NMR studies of adduct **4** were impossible because of its very low yield. The struc-

Scheme 3



Reagents and conditions: *o*-DCB, 180 °C, 2.5 h.

ture of adduct **5** was confirmed by its ^{1}H and ^{13}C NMR spectra.

In the ^{1}H NMR spectrum of adduct **5**, the H(5) and H(8) atoms of the fluoroquinoxaline fragment are manifested as the doublets at δ 8.30 ($^4J_{H,F}$ = 8.2 Hz) and 8.02 ($^3J_{H,F}$ = 11.2 Hz). Both the doublets are shifted downfield compared to the analogous signals in the spectrum of azide **2**, especially for the H(5) atom. The positions of the signals for the H(2) and H(3) atoms of the pyrazine ring are insignificantly affected by the presence of the fullerene sphere in adduct **5**.

The number of lines in the ^{13}C NMR spectrum of adduct **5** in the δ range from 140 to 145 ppm (3 2C, 9 4C, and 2 8C) suggests that its symmetry (C_{2v}) is as high as in adduct **3**. However, the signal for the sp^3-hybridized C atoms of the sphere in the ^{13}C NMR spectrum of adduct **5** is shifted downfield (δ 101.14) compared to the signal for the analogous C atoms in adduct **3** (δ 84.13). This can be associated with the stronger electron-withdrawing effect of the fluoroquinoxaline fragment on the fullerene sphere than is produced by the fluoronitrophenyl substituent. The quinoxaline fragment is retained in adduct **5**, which is indicated by the characteristic signals in its ^{13}C NMR spectrum.

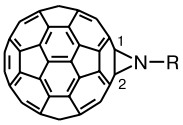
Thus, the above physicochemical data suggest that the reaction of C_{60} with 6-azido-7-fluoroquinoxaline (**2**) gives 7-fluoro-6-{[60]fullereno[1,2-*b*]aziridino}quinoxaline (**5**) as the major monoadduct and 6-{azahomo[60]fullereno}-7-fluoroquinoxaline (**4**) as the minor adduct.

Interestingly, monoadducts **3** and **5** have, on the NMR scale, the high symmetry C_{2v}, which is far from being characteristic of all fullerenoaziridines.[9] Our DFT/PBE/TZ2P quantum-chemical calculations with the PRIRODA program[10,11] showed that such a symmetry is most likely due to the pyramidal inversion of the N atom in the exohedral aziridine ring.

Note that the DFT/PBE/TZ2P-calculated inversion barriers of the N atom in amines and aziridines are close to experimental data.[12] For instance, the theoretical inversion barriers in trimethylamine, aziridine, and *N*-methylaziridine are 35.8, 74.8, and 75.3 kJ mol^{-1}, respectively. The fusion of the aziridine ring with the fullerene sphere for R = H and Me lowers the inversion barrier of the N atom from 75 to ~50 kJ mol^{-1}, while for R = Ph, the barrier is further reduced by half (Table 1). Introduction of a nitro group into the phenyl substituent additionally lowers the inversion barrier. As the result, at the barrier ΔE ~25 kJ mol^{-1}, the inversion of nitrogen in monoadduct **3** is so rapid that particular inverted forms are undetectable by the NMR method.

It should also be noted that lowering of the inversion barrier in fullerenoaziridines compared to aziridines involves substantial lengthening of the aziridine C(1)—C(2) bond in the transition structure, which increases the C(1)—N—C(2) angle and thus makes the transition structure much less strained (see Table 1). Conjugation of the aziridine N atom with the phenyl ring, which is most efficient in the planar transition structure, stabilizes this structure and additionally lowers the inversion barrier.

Table 1. Inversion barriers ΔE of nitrogen and the lengths of the acyclic N—C bond and the C—C bond of the aziridine ring for some [60]fullereno[1,2-*b*]aziridines



Compound	ΔE /kJ mol^{-1}	*d*/Å	
		N—C	C(1)—C(2)
R, H	56.4	1.027*	1.592
		(1.008)	(2.031)
R, Me	51.1	1.468	1.605
		(1.447)	(2.010)
R, Ph	27.7	1.42	1.602
		(1.396)	(2.036)
R, $C_6H_4NO_2$-4	20.8	1.408	1.607
		(1.384)	(2.053)
R, 2-fluoro-4-nitrophenyl	25.4	1.404	1.598
		(1.372)	(1.712)

Note. The data for the planar transition structure are enclosed in parentheses.
* The N—H bond.

The electrochemical properties of adducts **3** and **5** were studied at room temperature by cyclic voltammetry (CVA). The results obtained were compared with CVA data for unsubstituted C_{60} and the starting azides **1** and **2**.

The CVA curve of the starting C_{60} under the conditions involved shows four reversible one-electron reduction peaks; their potentials are given in Table 2. Azides **1** and **2** are reduced in the same potential range as for C_{60}. The voltammograms of both azides contain two irreversible reduction peaks (see Table 2). It is known that addition of two electrons to nitrobenzene in highly diluted solutions is accompanied by protonation of the anionic centers to form *N*-hydroxyaniline.[13] Under analogous conditions, electrochemical reduction of quinoxalines yields 1,4-dihydroquinoxalines through addition to two C=N bonds.[13] Most probably, analogous processes occurs during the reduction of azides **1** and **2**.

The cyclic voltammograms of adducts **3** and **5** contain five and four reduction peaks, respectively (see Table 2). For adduct **5**, the first reduction peak was reversible only when the potential was swept to the end of the first polarographic wave, while for adduct **3**, the first two peaks were reversible on the reverse scan of the potential from the end of the second wave. Potential sweeping from 0 to 2.5 V makes all the reduction peaks irreversible in the

Table 2. Peak potentials (E/V) and currents (I/μA) in the CVA curves of C_{60} and compounds **1**—**3** and **5**

Compound	$-E_{p,1}^{red}$ (I_p^{red})	$-E_{p,2}^{red}$ (I_p^{red})	$-E_{p,3}^{red}$ (I_p^{red})	$-E_{p,4}^{red}$ (I_p^{red})	$-E_{p,5}^{red}$ (I_p^{red})
C_{60}	0.83*	1.24*	1.70*	2.16*	—
	(4.2)	(3.8)	(3.9)	(4.6)	
1	1.24	2.01	—	—	—
	(26.5)	(22.5)			
2	1.57	2.22	—	—	—
	(18.5)	(13.0)			
3	0.82	1.23	1.76	2.01	2.16
	(3.2)	(5.3)	(5.0)	(3.3)	(2.0)
5	0.82	1.26	1.70	2.25	—
	(7.3)	(12.5)	(6.8)	(10.8)	

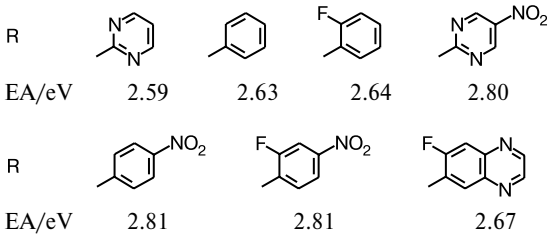
* The reversible reduction peaks.

CVA curves of both adducts. The reduction irreversibility for adducts **3** and **5** is most likely due to protonation of the anionic centers formed by electron transfer to the fluoronitrophenyl or fluoroquinoxaline fragments rather than to opening of the aziridine rings fused with the fullerene sphere since these rings were found to be unaffected by electrochemical reduction of fullerenoaziridines.[9,14]

Comparison of the reduction potentials and currents in the CVA curves of adduct **3**, the starting C_{60}, and arylazide **1** allows a conclusion that the first peak corresponds to transfer of one electron to the fullerene sphere to form a monoanion. The increase in the current of the second peak is probably associated with simultaneous reduction of the fullerene sphere and the nitro group of the phenyl radical. The subsequent three peaks correspond to transfer of three electrons to the nitrophenyl fragment of azide **1**; both the sphere and the nitro group are reduced, with accompanying protonation of the anionic centers of the latter.

In the case of adduct **5**, the first electron is also transferred to the fullerene sphere to form a monoanion. The two-electron character of the second and fourth peaks indicates simultaneous reduction of the fullerene and quinoxaline fragments of adduct **5**. At the potential of the third reduction peak, one electron is most probably transferred only to the fullerene sphere. Note that transfer of the first electron to the quinoxaline ring occurs at the higher potential (−1.26 V) compared to azide **2** (−1.57 V).

The potentials of the first reduction peaks of the starting C_{60} and adducts **3** and **5** are very close, although bond saturation in these adducts should diminish the electron affinity (EA) of the fullerene fragments relative to the EA of nonmodified fullerene. Obviously, such an electrochemical behavior of adducts **3** and **5** is due to the presence of the electron-withdrawing N atom adjacent to the fullerene sphere, the electron-withdrawing effects of the substituents in the phenyl fragment, and the electron-deficient character of the quinoxaline bicycle. This conclusion was confirmed by PM3-calculations of EA for some [60]fullereno[1,2-*b*]aziridines. The electron affinities obtained from the LUMO energies and scaled with respect to the experimental EA value of fullerene C_{60} (2.65 eV) are given below.



It can be seen that the electron affinity of adduct **3** should be higher than the affinity of nonmodified fullerene. The EA of fullerenoaziridine is strongly affected only by the N atom of the nitro group in the organic substituent R, while the effect of the fluorine atom is insignificant. However, it is worth noting that the calculations point only to an expected tendency toward an increase in the EA of fullerenoaziridines.

Thus, attachment of the fluoronitrophenyl and fluoroquinoxaline fragments to the fullerene surface through an aziridine ring makes it possible to create a covalently bonded fullerene-containing dyad C_{60}—acceptor, in which the fullerene sphere is not inferior to nonmodified C_{60} in electron affinity.

Experimental

IR spectra were recorded on a Bruker IFS-113V Fourier spectrometer (KBr pellets). ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250.13 MHz) with Me_4Si as the internal standard. ^{13}C NMR spectra were recorded on a Bruker MSL-400 instrument (100.62 MHz). The δ values were referenced to Me_4Si. UV spectra were recorded on a Specord UV-VIS instrument. The mass spectrum of adduct **3** was recorded on a MALDI TOF MS instrument (Dynamo) with the use of a nitroaniline matrix. The mass spectra of adducts **4** and **5** were recorded on a Finnigan MAT 212 mass spectrometer with a MASPEC II32 system for data processing (direct inlet probe, heated ion source, voltage 60 eV, electron emission current 0.5 mA). In cyclic voltammetry, a stationary glassy carbon disk electrode (working area 3.14 mm^2) was used as a measuring electrode. Voltammograms (CVA curves) were recorded in a three-electrode electrochemical cell connected to a PI-50-1 potentiostat fitted with a PR-8 programmer (linear potential sweep rate 50 mV s^{-1}). The solvent was *o*-DCB—MeCN (3 : 1) with 0.1 *M* Bu_4NBF_4 as a supporting electrolyte. The reference electrode was Ag/0.01 *M* $AgNO_3$ in MeCN. A platinum wire was used as an auxiliary electrode. Measurements were performed in a temperature-controlled (25 °C) cell under argon. The concentrations of C_{60}, azides **1** and **2**, and adduct **3**

were $1 \cdot 10^{-3}$ mol L^{-1}. The concentration of adduct **5** was $2 \cdot 10^{-3}$ mol L^{-1}. *o*-Dichlorobenzene and MeCN were dried by distillation over P_2O_5. [60]Fullerene was prepared at the G. A. Razuvaev Institute of Organometallic Chemistry of the Russian Academy of Sciences (Nizhny Novgorod).

Elemental analysis was performed with an Analizator CHN-3 instrument.

1-Azido-2-fluoro-4-nitrobenzene (1) was prepared as described earlier.[15] Found (%): C, 39.06; H, 1.77; N, 30.30. $C_6H_3FN_4O_2$. Calculated (%): C, 39.57; H, 1.66; N, 30.77. IR (KBr), ν/cm^{-1}: 2135, 2104 (N_3), 1522, 1349, 742 (NO_2), 3105, 3015, 3054, 1598, 1496 (phenyl), 1310 (C—F). UV (CH_2Cl_2), λ_{max}/nm: 226, 314. ^{1}H NMR ($CDCl_3$), δ: 7.19 (dd, 1 H, H(6), $^4J_{H,F}$ = 8.5 Hz, $^3J_{H,H}$ = 8.5 Hz); 8.01 (dd, 1 H, H(5), $^3J_{H,H}$ = 8.5 Hz, $^4J_{H,H}$ = 2.5 Hz); 8.05 (dd, 1 H, H(3), $^3J_{H,F}$ = 12.7 Hz, $^4J_{H,H}$ = 2.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 113.09 (ddd, C(3), $^1J_{C,H}$ = 170.5 Hz, $^2J_{C,F}$ = 24.6 Hz, $^3J_{C,H}$ = 5.0 Hz); 120.88 (ddm, C(5), $^1J_{C,H}$ = 171.3 Hz, $^2J_{C,F}$ = 3.5 Hz); 121.26 (dm, C(6), $^1J_{C,H}$ = 167.0 Hz); 135.5 (dm, C(1), $^2J_{C,F}$ = 10.1 Hz); 144.71 (m, C(4)); 154.13 (dm, C(2), $^1J_{C,F}$ = 253.5 Hz).

6-Azido-7-fluoroquinoxaline (2). A solution of sodium nitrite (1.21 g, 17.5 mmol) in water (12 mL) was added in portions to a suspension (cooled to 0 °C) of 7-fluoro-6-hydrazinoquinoxaline (2.67 g, 15.2 mmol) in 18% HCl (50 mL) in such a way that the reaction temperature did not exceed 0 to 3 °C. After one hour, the precipitate that formed was filtered off, washed with water, and recrystallized from aqueous ethanol. The yield of compound **2** was 1.8 g (63%), m.p. 105—106 °C. Found (%): C, 50.66; H, 2.17; N, 36.73. $C_8H_4FN_5$. Calculated (%): C, 50.79; H, 2.13; N, 37.09. IR (KBr), ν/cm^{-1}: 2082, 2106 (N_3), 3022, 3043, 1620, 1503 (quinoxaline), 1323 (C—F). UV (CH_2Cl_2), λ_{max}/nm: 249, 333, 345. ^{1}H NMR ($CDCl_3$), δ: 7.78 (d, 1 H, H(8), $^3J_{H,F}$ = 10.0 Hz); 7.81 (d, 1 H, H(5), $^4J_{H,F}$ = 8.2 Hz); 8.80 (d, 1 H, H(2) or H(3), $^3J_{H,H}$ = 3.4 Hz); 8.81 (d, 1 H, H(3) or H(2), $^3J_{H,H}$ = 3.4 Hz). ^{13}C NMR ($CDCl_3$), δ: 114.69 (dd, C(8), $^1J_{C,H}$ = 167.5 Hz, $^2J_{C,F}$ = 18.8 Hz); 119.49 (dd, C(5), $^1J_{C,H}$ = 166.0 Hz, $^3J_{C,F}$ = 2.3 Hz); 133.35 (dm, C(6), $^2J_{C,F}$ = 15.2 Hz); 141.02 (m, C(4a)); 141.49 (dm, C(8a), $^3J_{C,F}$ = 12.0 Hz); 145.12 (dd, C(3), $^1J_{C,H}$ = 183.1 Hz, $^2J_{C,H}$ = 12.0 Hz); 145.31 (ddd, C(2), $^1J_{C,H}$ = 183.0 Hz, $^2J_{C,H}$ = 11.0 Hz, $^5J_{C,F}$ = 4.0 Hz); 156.04 (dm, C(7), $^1J_{C,F}$ = 258.2 Hz).

1-(2-Fluoro-4-nitrophenyl)[60]fullereno[1,2-*b*]aziridine (3). Azide **1** (56 mg, 0.308 mmol) was added to a solution of C_{60} (109 mg, 0.152 mmol) in dry *o*-DCB (25 mL). The reaction mixture was stirred at 180 °C for 2 h and concentrated *in vacuo*. The residue was chromatographed on silica gel. With toluene as an eluent, a fraction containing a mixture of adduct **3** and the unreacted fullerene and fractions containing mixtures of isomeric polyadducts were isolated. Adduct **3** was separated from fullerene by repeated chromatography with toluene—light petroleum (1 : 1) as an eluent. The yield of adduct **3** was 24 mg (18%), R_f 0.9 (toluene) and 0.50 (toluene—light petroleum, 1 : 1). Found (%): N, 3.47. $C_{66}H_3FN_2O_2$. Calculated (%): N, 3.20. MS, *m/z*: found 720 (C_{60}); 874 ($C_{66}H_3FN_2O_2$); calculated 874. IR (KBr), ν/cm^{-1}: 1523, 1338, 740 (NO_2), 3078, 1601, 1494 (phenyl), 1315 (C—F), 526 (fullerene). UV (CH_2Cl_2), λ_{max}/nm: 255, 324, 421, 457, 670. ^{1}H NMR ($CDCl_3$), δ: 7.81 (dd, 1 H, H(6), $^4J_{H,F}$ = 8.3 Hz, $^3J_{H,H}$ = 8.3 Hz); 8.27—8.23 (m, 2 H, H(3), H(5)). ^{13}C—{^{1}H} NMR ($CDCl_3$), δ: phenyl fragment: 113.45 (d, C(3), $^2J_{C,F}$ = 23.1 Hz); 120.70 (d, C(6), $^4J_{C,F}$ = 5.0 Hz); 123.42 (br.s, C(5)); 140.62 (d, C(1), $^2J_{C,F}$ = 22.1 Hz); 143.25 (br.s, C(4)); 154.8 (d, C(2), $^1J_{C,F}$ = 236.8 Hz); C_{60}N: 84.13 (2 C), 140.96 (4 C), 141.55 (4 C), 142.48 (4 C), 142.52 (4 C), 143.97 (4 C), 144.24 (2 C), 144.31 (4 C), 144.77 (4 C), 145.03 (4 C), 145.41 (4 C), 145.52 (4 C), 145.71 (4 C), 145.79 (4 C), 143.58 (8 C).

Reaction of C_{60} with azide 2. Azide **2** (29 mg, 0.164 mmol) was added to a solution of C_{60} (79 mg, 0.110 mmol) in dry *o*-DCB (25 mL). The reaction mixture was stirred at 180 °C for 2.5 h and concentrated *in vacuo*. The residue was chromatographed on silica gel with toluene as an eluent to give C_{60} (16 mg, 20%), adduct **4** (3 mg, 3%), adduct **5** (13 mg, 13%), and fractions containing mixtures of isomeric polyadducts.

6-{Azahomo[60]fullereno}-7-fluoroquinoxaline (4), R_f 0.32 (toluene). Found (%): N, 4.82. $C_{68}H_4FN_3$. Calculated (%): N, 4.76. MS, *m/z*: found 720.0 (C_{60}); 881.0 ($C_{68}H_4FN_3$); calculated 720.0 (C_{60}); 881.736. IR (KBr), ν/cm^{-1}: 3093, 1620, 1511 (quinoxaline), 1316 (C—F), 526 (fullerene). UV (CH_2Cl_2), λ_{max}/nm: 255, 315, 430 (broad).

7-Fluoro-6-{[60]fullereno[1,2-*b*]aziridino}quinoxaline (5), R_f 0.26 (toluene). Found (%): N, 4.71. $C_{68}H_4FN_3$. Calculated (%): N, 4.76. MS, *m/z*: found 720.1 (C_{60}); 880.9 ($C_{68}H_4FN_3$); calculated 720.0 (C_{60}); 881.736. IR (KBr), ν/cm^{-1}: 3022, 3043, 1621, 1492 (quinoxaline), 1321 (C—F), 526 (fullerene). UV (CH_2Cl_2), λ_{max}/nm: 252, 325, 425 (narrow), 492, 662. ^{1}H NMR ($CDCl_3$), δ: 8.02 (d, 1 H, H(8), $^3J_{H,F}$ = 11.2 Hz); 8.30 (d, 1 H, H(5), $^4J_{H,F}$ = 8.2 Hz); 8.85 (d, 1 H, H(3), $^3J_{H,H}$ = 3.0 Hz); 8.87 (d, 1 H, H(2), $^3J_{H,H}$ = 3.0 Hz). ^{13}C—{^{1}H} NMR ($CDCl_3$), δ: 114.69 (d, C(8), $^2J_{C,F}$ = 18.6 Hz); 121.64 (d, C(5), $^3J_{C,F}$ = 3.0 Hz); 141.50 (d, C(6), $^2J_{C,F}$ = 12.0 Hz); 140.73 (s, C(4a)); 140.88 (d, C(8a), $^3J_{C,F}$ = 11.1 Hz); 145.26 (s, C(3)); 145.38 (br.s, C(2)); 156.90 (d, C(7), $^1J_{C,F}$ = 254.8 Hz); C_{60}N: 101.14 (2 C), 143.21 (2 C), 145.26 (2 C), 145.38 (2 C), 141.10 (4 C), 141.50 (4 C), 143.54 (4 C), 143.58 (4 C), 144.31 (4 C), 144.41 (4 C), 145.47 (4 C), 145.67 (4 C), 145.75 (4 C), 142.55 (8 C), 144.99 (8 C).

This work was financially supported by the Russian Foundation for Basic Research (Project Nos 02-03-32932 and 03-03-32254), the Ministry of Science, Industry, and Technology of the Russian Federation (MK-749.2003.03), and the Russian Academy of Sciences (Program of the Division of Chemistry and Materials Sciences of the Russian Academy of Sciences No. 7-OKh).

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Received November 16, 2004;
in revised form March 11, 2005